

This Page Is Inserted by IFW Operations  
and is not a part of the Official Record

## **BEST AVAILABLE IMAGES**

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images may include (but are not limited to):

- BLACK BORDERS
- TEXT CUT OFF AT TOP, BOTTOM OR SIDES
- FADED TEXT
- ILLEGIBLE TEXT
- SKEWED/SLANTED IMAGES
- COLORED PHOTOS
- BLACK OR VERY BLACK AND WHITE DARK PHOTOS
- GRAY SCALE DOCUMENTS

**IMAGES ARE BEST AVAILABLE COPY.**

**As rescanning documents *will not* correct images,  
please do not report the images to the  
Image Problem Mailbox.**

## SPECIFICATION

### PROCESS FOR REFINING RAW COPPER MATERIAL CONTAINING COPPER SULFIDE MINERAL

#### BACKGROUND OF THE INVENTION

#### FIELD OF THE INVENTION

The present invention relates to a process for refining a raw copper material containing a copper sulfide mineral, more particularly a hydrometallurgical refining process for a raw copper material containing a copper sulfide mineral, e.g., chalcopyrite, which can leach copper out of the raw material at a high extraction while suppressing oxidation of sulfur, recover it in the monovalent state by electrolysis and, at the same time, recover a concomitant valuable metal while minimizing production of wastes, e.g., leaching residue, as far as possible.

#### DESCRIPTION OF THE PRIOR ART

At present, copper has been produced mostly by a pyrometallurgical process worldwide, which treats a copper concentrate as the starting material. The copper concentrate is produced from a copper sulfide mineral, e.g., chalcopyrite ( $\text{CuFeS}_2$ ), chalcocite ( $\text{Cu}_2\text{S}$ ) or bornite ( $\text{Cu}_5\text{FeS}_4$ ), by a physical separation process, e.g., floatation, which concentrates the copper sulfide mineral. The copper concentrate composition, depending mostly on the site in which the ore is occurring, contains, in addition to a copper sulfide mineral, an iron sulfide mineral (e.g., iron pyrite, pyrrhotite or the like) and oxide mineral (e.g., silicate mineral as gangue). Moreover, it also contains zinc, lead, a mineral of Group 5 element in the periodic table (e.g., arsenic, antimony, bismuth or the like), mineral of Group 6 element in the periodic table (e.g., selenium, tellurium or the like) and noble metal,

present mostly in the sulfide mineral.

The pyrometallurgical process for copper refining electrolytically refines crude copper produced by a series of pyrometallurgical refining steps which use a smelting furnace, converter, refining furnace or the like to treat a copper concentrate. It is suitable for efficient treatment of large quantities of copper ore. However, it involves several problems. For example, it needs a huge investment for large-size facilities because of insufficient reaction efficiency by small-size facilities, and must be provided with a system for recovering massively produced SO<sub>2</sub> gas.

Under these circumstances, hydrometallurgical processes have been studied recently for copper refining. The conventional hydrometallurgical copper refining process widely used on an industrial scale involves spraying sulfuric acid onto a piled copper ore containing a copper oxide mineral to leach out copper, solvent extraction to increase copper concentration of the leaching product liquor, and electrolysis to recover copper. However, this process involves problems, when applied to refining a sulfide ore, which accounts for the greater part of copper ore. Taking chalcopyrite, which is occurring more massively than any other copper sulfide, as an example, it is leached by sulfuric acid at a slow rate, resulting in low copper extraction. It is therefore difficult for the hydrometallurgical process to secure productivity comparable with that of the pyrometallurgical process for refining a raw copper material containing chalcopyrite.

Processes adopting conditions under which chalcopyrite leaching is promoted have been proposed to solve the above problems. One of the more representative processes involves oxidation of a copper ore or concentrate under pressure in a halide-containing sulfuric acid solution, leaching of the

treated ore or concentrate, solvent extraction of the leaching product liquor, and electrolysis to recover copper from the stripping solution containing cupric ion (disclosed by, e.g., Patent Document 1). Another representative process involves leaching of a copper concentrate with a leachate capable of forming a halide complex, e.g.,  $\text{BrCl}_2^-$ , and electrolysis of the leaching product liquor containing cuprous ion which has undergone leaching at a low oxidation-reduction potential to recover copper (disclosed by, e.g., Patent Document 2).

The hydrometallurgical refining process has several advantages over the pyrometallurgical process, e.g., relatively simple process and hence reduced investment, because it operates at a lower reaction temperature and can be cyclically started and stopped in a shorter time, which makes production schedule adjustment more flexible. However, the hydrometallurgical refining process still involves the following problems to be solved to further improve efficiency.

(1) Higher copper extraction with chalcopyrite, and suppressed oxidation of sulfur

The hydrometallurgical process preferably recovers sulfur from a sulfide mineral in the form of elemental sulfur, which can be stored more easily than sulfuric acid. However, sulfur tends to be oxidized in the leaching step, when chalcopyrite, which is difficult to extract, is leached under a strongly oxidative atmosphere to attain a high copper extraction, and cannot be efficiently recovered in the form of elemental sulfur, because it is eluted out as the sulfate ion in the leaching solution. Therefore, there are demands for leaching processes which treat chalcopyrite at a high extraction and, at the same time, realize suppressed oxidation of sulfur.

## (2) Efficient reduction of copper

The hydrometallurgical process preferably recovers copper by electrolysis from an aqueous chloride solution containing cuprous ion. More specifically, copper is present only in the divalent state in a sulfuric acid solution, whereas it may be monovalent or divalent in a chloride solution. The electrolysis of cuprous ion (i.e., monovalent copper) is more economical than that of divalent copper, because its power consumption is halved. It should be noted, however, that the copper ion is present in the form of divalent state in the leach solution from the leaching step which uses chlorine gas, because of high oxidation-reduction potential of the solution. It is known that divalent copper has been reduced into monovalent one by blowing  $\text{SO}_2$  gas as a reductant into the system or recycling part of the copper powder recovered by electrolysis. However,  $\text{SO}_2$  gas increases concentration of the sulfate ion in the leaching product liquor, to push up the solution treatment cost. On the other hand, use of the copper powder directly decreases the product yield by the quantity it is recycled, which also pushes up the cost. Therefore, development of efficient processes for reducing the copper ion has been demanded for electrolysis of monovalent copper.

## (3) Reduction of residue wastes and efficient recovery of iron

The residue exhausted from the hydrometallurgical leaching process is generally more chemically unstable than slag from the pyrometallurgical refining process, and concerns of the residue-containing impurities eluted into the ambient environments have been pointed out. It is desirable to improve extraction of iron as the major ingredient of the leaching residue and recover the iron in the utilizable form as the countermeasures to decrease residue wastes.

Under these situations, there are demands for hydrometallurgical refining processes which can solve the problems involved in the conventional processes to efficiently treat a raw copper material containing a copper sulfide mineral.

The average particle size (D50) described in this specification was determined by a Microtrac particle size distribution analyzer (Nikkiso Co., 9320HRA (X-100)).

[Patent Document 1]

Japanese Patent Laid-open Publication No.2001-515145 (Pages 1 and 2)

[Patent Document 2]

Japanese Patent No.2,857,930 (Pages 1 to 4)

**SUMMARY OF THE INVENTION**

It is an object of the present invention to provide a hydrometallurgical process for refining a raw copper material containing a copper sulfide mineral, e.g., chalcopyrite, which can leach copper out of the raw material at a high extraction while suppressing oxidation of sulfur, recover it in the monovalent state by electrolysis and, at the same time, recover a concomitant valuable metal while minimizing production of wastes, e.g., leaching residue, as far as possible, in consideration of the problems involved in the conventional processes.

The inventors of the present invention have found, after having extensively studied processes for refining a raw copper material containing a copper sulfide mineral, that a process can efficiently separate and recover copper, iron and a concomitant valuable metal when it comprises a series of steps for leaching a raw copper material containing a copper sulfide mineral in the presence of chlorine in an acidic, aqueous chloride solution, reduction

of the copper ion in the leaching product liquor, extraction of copper from the reduction product liquor with the aid of solvent followed by stripping of the extract with the aid of a solvent, electrolysis for recovering copper, and electrolysis for recovering iron, achieving the present invention.

The first aspect of the present invention is a process for refining raw copper material containing copper sulfide mineral characterized by a hydrometallurgical process for recovering copper and a concomitant valuable metal from a raw copper material containing a copper sulfide mineral, comprising:

- (1) a chlorine-aided leaching step for leaching the raw copper material in the presence of chlorine in an acidic, aqueous chloride solution to produce the leaching product liquor containing the copper ion and residue containing elemental sulfur by leaching copper in the acidic solution,
- (2) a copper ion reduction step for reducing the leaching product liquor in the presence of a reductant to produce the reduction product liquor containing the cuprous ion,
- (3) a solvent extraction step for extracting copper with the aid of solvent from the reduction product liquor, and stripping loaded solvent to produce the stripping product liquor containing the cuprous ion and raffinate containing the ferrous ion,
- (4) a copper electrowinning step for electrolyzing the stripping product liquor to produce the electrolytic copper and spent electrolyte, and
- (5) an iron electrowinning step for electrolyzing the raffinate to produce the electrolytic iron and iron spent electrolyte composed of the aqueous iron chloride solution.

The second aspect of the present invention is the process of the first aspect for refining a raw copper material containing a copper sulfide

mineral, wherein the chlorine-aided leaching step is effected by blowing chlorine gas into the acidic, aqueous chloride solution.

The third aspect of the present invention is the process of the first aspect for refining a raw copper material containing a copper sulfide mineral, wherein the chlorine-aided leaching step is effected at a slurry concentration of 100 to 400g/L, leaching temperature of 100 to 110°C and oxidation-reduction potential of 500 to 600mV (based on an Ag/AgCl electrode).

The fourth aspect of the present invention is the process of the first aspect for refining a raw copper material containing a copper sulfide mineral, wherein the chlorine-aided leaching step is controlled in such a way to have a final chloride ion concentration of 250 to 400g/L in the acidic, aqueous chloride solution.

The fifth aspect of the present invention is the process of the first aspect for refining a raw copper material containing a copper sulfide mineral, wherein the copper ion reduction step uses the copper sulfide mineral as the reductant.

The sixth aspect of the present invention is the process of the fifth aspect for refining a raw copper material containing a copper sulfide mineral, wherein the copper sulfide mineral is treated under heating at the atmospheric pressure in the leaching product liquor to produce the reduction product liquor and residue containing elemental sulfur.

The seventh aspect of the present invention is the process of the sixth aspect for refining a raw copper material containing a copper sulfide

mineral, wherein the copper sulfide mineral is a copper concentrate mainly composed of chalcopyrite, prepared to have an average particle diameter (D50) of 0.5 to 60 $\mu\text{m}$ , and temperature at which the leaching product liquor is reduced is 90 to 110°C and, at the same time, is at least the temperature level (A) given by the following formula 1:

Formula 1:  $A(\text{°C}) = 6.79 \times \ln(B) + 81.5$

(wherein, B is an average particle diameter (D50,  $\mu\text{m}$ ), determined by the Microtrac analyzer, at a volumetric cumulative frequency of 50% of the copper concentrate).

The eighth aspect of the present invention is the process of the sixth aspect for refining a raw copper material containing a copper sulfide mineral, wherein the copper sulfide mineral is a copper concentrate mainly composed of chalcopyrite, prepared to have an average particle diameter (D50) of 0.5 to 60 $\mu\text{m}$ , and temperature at which the leaching product liquor is reduced is 90 to 110°C and, at the same time, is at least the temperature level (A) given by the following formula 2:

Formula 2:  $A(\text{°C}) = 7.04 \times \ln(B) + 95.2$

(wherein, B is an average particle diameter (D50,  $\mu\text{m}$ ), determined by the Microtrac analyzer, at a volumetric cumulative frequency of 50% of the copper concentrate).

The ninth aspect of the present invention is the process of the sixth aspect for refining a raw copper material containing a copper sulfide mineral, wherein the residue is recycled back as a raw copper material to the chlorine-aided leaching step.

The tenth aspect of the present invention is the process of the first aspect for refining a raw copper material containing a copper sulfide

mineral, wherein the solvent extraction step uses an organic solvent containing a solvating extractant for solvent extraction.

The 11<sup>th</sup> aspect of the present invention is the process of the tenth aspect for refining a raw copper material containing a copper sulfide mineral, wherein the organic solvent contains the solvating extractant at 40% by volume or more.

The 12<sup>th</sup> aspect of the present invention is the process of the first aspect for refining a raw copper material containing a copper sulfide mineral, wherein an aqueous solution for stripping in the solvent extraction step contains copper at 70g/L or less and chlorine ion at 50 to 350g/L.

The 13<sup>th</sup> aspect of the present invention is the process of the first aspect for refining a raw copper material containing a copper sulfide mineral, wherein the stripping is effected at 40 to 90°C in the solvent extraction step.

The 14<sup>th</sup> aspect of the present invention is the process of the first aspect for refining a raw copper material containing a copper sulfide mineral, wherein the copper electrowinning step is effected in an electrolysis tank composed of a cathode chamber and anode chamber separated from each other by a diaphragm, characterized in that the stripping product liquor containing the cuprous ion, discharged from the solvent extraction step, is supplied to the cathode chamber to electrowin copper on the cathode, the iron spent electrolyte composed of an aqueous iron chloride solution, discharged from the iron electrowinning step, is supplied to the anode chamber for anodic oxidation, and the solution being supplied to the anode chamber is prevented from flowing into the cathode chamber through the diaphragm.

The 15<sup>th</sup> aspect of the present invention is the process of the 14<sup>th</sup> aspect for refining a raw copper material containing a copper sulfide mineral, wherein water permeates through the diaphragm at 0.04 to 0.15L/m<sup>2</sup>·s.

The 16<sup>th</sup> aspect of the present invention is the process of the 14<sup>th</sup> aspect for refining a raw copper material containing a copper sulfide mineral, wherein the cathode and anode chambers in the electrolysis tank are structured in such a way that a solution is charged and discharged separately in each chamber, and the solution level is kept higher in the cathode chamber than in the anode chamber.

The 17<sup>th</sup> aspect of the present invention is the process of the 14<sup>th</sup> aspect for refining a raw copper material containing a copper sulfide mineral, wherein the solution discharged from the cathode chamber is recycled back as the stripping solution to the solvent extraction step, and the solution discharged from the anode chamber is recycled back as the leachate to the chlorine-aided leaching step.

The 18<sup>th</sup> aspect of the present invention is the process of the first aspect for refining a raw copper material containing a copper sulfide mineral, wherein the iron electrowinning step is effected in an electrolysis tank composed of an anode chamber and cathode chamber separated from each other by a filter cloth, characterized in that the iron ion is supplied to the anode chamber at a rate at least twice as high as that for the iron ion deposited on the cathode in order to decrease cell voltage.

The 19<sup>th</sup> aspect of the present invention is the process of the first aspect for refining a raw copper material containing a copper sulfide mineral,

wherein a solution purification step is included upstream of the iron electrowinning step to purify the raffinate from the solvent extraction step, which produces the purified solution and precipitate product.

The 20<sup>th</sup> aspect of the present invention is the process of the 19th aspect for refining a raw copper material containing a copper sulfide mineral, wherein the raffinate from the solvent extraction step is purified in the solution purification step by a treatment method selected from the group consisting of sulfidation, cementation and neutralization.

The 21<sup>st</sup> aspect of the present invention is the process of the first aspect for refining a raw copper material containing a copper sulfide mineral, wherein the residue containing elemental sulfur, discharged from the chlorine-aided leaching step, is distilled in an inert atmosphere to be separated into the condensed sulfur and residue containing a concomitant metal, after evaporating sulfur.

The 22<sup>nd</sup> aspect of the present invention is the process of the first aspect for refining a raw copper material containing a copper sulfide mineral, wherein the electrolytic copper produced in the copper electrowinning step is used as the anode to be refined by electrolysis and separated into the high-purity, electrolytic copper and silver-containing slime.

The process of the present invention as a hydrometallurgical process for refining a raw copper material containing a copper sulfide mineral, e.g., chalcopyrite, can leach copper out of the raw material at a high extraction while suppressing oxidation of sulfur, recover it in the monovalent state by electrolysis and, at the same time, recover a concomitant valuable metal while minimizing production of wastes, e.g., leaching residue, as far as

possible, and hence is of high industrial value.

#### BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 shows one embodiment of the refining process scheme of the present invention.

Figure 2 shows the relationship between the copper ion state (cuprous/cupric concentration ratio, Cu(1)/Cu(2)) and ORP (based on an Ag/AgCl electrode), where the chloride solution was incorporated with a varying concentration of ferrous ion at 90°C.

Figure 3 shows the relationships among reduction temperature, particle size and ORP level (based on an Ag/AgCl electrode), where the reduction was effected under varying reduction temperature and particle size.

Figure 4 shows the relationship (obtained by the regression analysis) between temperature and particle size (D50) at a target ORP level (based on an Ag/AgCl electrode) of 400mV.

Figure 5 shows the relationship (obtained by the regression analysis) between temperature and particle size (D50) at a target ORP level (based on an Ag/AgCl electrode) of 380mV.

Figure 6 illustrates one structural embodiment of the electrolysis tank for the present invention.

Figure 7 shows the effects of slurry concentration in the chlorine-aided leaching step on copper and iron extraction, and sulfur oxidation.

Figure 8 shows the effects of the final chlorine ion concentration in the chlorine-aided leaching step on copper and iron extraction, and sulfur oxidation.

Figure 9 shows the effects of tributyl phosphate concentration in the solvent extraction step on copper and iron extraction.

Figure 10 shows the effects of tributyl phosphate concentration in the solvent extraction step on copper/iron separation coefficient.

Figure 11 shows the effects of solution temperature in the solvent extraction step on stripping rate of copper.

#### NOTATION

- 1 Chlorine-aided leaching step
- 2 Copper ion reduction step
- 3 Solvent extraction step
- 4 Copper electrowinning step
- 5 Solution purification step
- 6 Iron electrowinning step
- 7 leaching residue treatment step
- 8 Raw copper material
- 9 Electrolytic copper
- 10 Electrolytic iron
- 11 Cathode chamber
- 12 Anode chamber
- 13 Diaphragm
- 14 Cathode
- 15 Anode
- 16 Overflow port in the cathode chamber
- 17 Overflow port in the anode chamber
- 18 Cathode supply solution
- 19 Anode supply solution
- 20 Catholyte
- 21 Anolyte
- 22 Spent catholyte
- 23 Spent anolyte

#### DETAILED DESCRIPTION OF THE INVENTION

The process of the present invention for refining a raw copper material containing a copper sulfide mineral is described in detail.

First, the process of the present invention for refining a raw copper material containing a copper sulfide mineral is outlined by referring to the attached drawings. Fig.1 shows one embodiment of the flow of the refining process of the present invention.

In Fig.1, the raw copper material 8 containing a copper sulfide mineral is first sent to the chlorine-aided leaching step 1, where it is separated into the leaching product liquor containing copper, iron and the like, and sulfur-containing residue. The product liquor is then sent to the copper ion reduction step 2, where copper in the solution is reduced to produce the reduction product liquor containing the cuprous ion. When the raw copper material containing a copper sulfide mineral is used as a reductant in this step, the residue from this step is recycled back to the chlorine-aided leaching step 1. The reduction product liquor is sent to the solvent extraction step 3, where it is separated into the stripping product liquor containing the cuprous ion and raffinate by the solvent extraction and stripping. The stripping product liquor is sent to the copper electrowinning step 4, where copper is recovered as the electrolytic copper 9.

Copper ores containing a copper sulfide mineral generally contain iron at a concentration comparable to that of copper, although varying depending on type of raw material for refining processes. This means that the raffinate from the solvent extraction step 3 contains a high concentration of iron ion. Therefore, the raffinate from the solvent extraction step 3 is sent to the solution purification step 5, as required, to be separated into the purified solution containing the iron ion and solid containing one or more types of valuable metals except iron. The purified solution containing the iron ion is sent to the iron electrowinning step 6,

where iron is recovered as the electrolytic iron 10.

The sulfur-containing residue separated in the chlorine-aided leaching step 1 is sent to the leaching residue treatment step 7, where elemental sulfur is recovered. The spent electrolytes separated in the copper electrowinning step 4 are recycled; the catholyte back to the solvent extraction step 3 as the solution for the stripping, and anolyte back to the chlorine-aided leaching step 1 as the leachate. The spent electrolyte from the iron electrowinning step 6 is recycled back to the copper electrowinning step 4 as the solution for the anode.

1. Raw copper material containing a copper sulfide mineral, and concomitant valuable metal

The raw copper materials containing a copper sulfide mineral, useful for the refining process of the present invention, include copper ores containing a copper sulfide mineral, e.g., chalcopyrite ( $\text{CuFeS}_2$ ), chalcocite ( $\text{Cu}_2\text{S}$ ) or bornite ( $\text{Cu}_5\text{FeS}_4$ ); copper concentrate in which a copper sulfide mineral is concentrated by treating the copper ore by floatation or the like; copper sulfide mineral; ores containing a varying copper mineral, e.g., copper oxide, copper arsenide or copper antimonide, and copper concentrate from the ore; copper matte, including high-quality copper matte, produced from a copper concentrate or the like by a pyrometallurgical refining process; and various raw copper materials, which are sulfide-like, oxide-like or metallic, when they are available to be treated together with the above.

The concomitant valuable metals include iron, nickel, cobalt, manganese, sulfur, zinc, cadmium, tin, lead, zinc, a Group 5 element in the periodic table (e.g., arsenic, antimony, bismuth or the like), Group 6 element in the periodic table (e.g., selenium, tellurium or the like), and noble metal.

## 2. Chlorine-aided leaching step

The chlorine-aided leaching step for the refining process of the present invention mainly leaches copper, iron and the like, in the presence of chlorine, out of a raw copper material containing a copper sulfide mineral, suspended in an acidic, aqueous chloride solution containing copper chloride, iron chloride or the like to produce the leaching product liquor containing the copper and iron ion and residue containing elemental sulfur by leaching copper, iron or the like. When the raw copper material is used as a reductant for the subsequent copper ion reduction step, it is preferable to use the residue from this step as the raw material for the leaching step. For example, the raw copper material may be totally treated in the copper ion reduction step to produce the raw copper material for the chlorine-aided leaching step.

Chlorine as the leaching solution for the above step is not limited, and a chlorine compound capable of oxidizing copper chloride, iron chloride or the like in the acidic, aqueous chloride solution is used. However, it is preferable to blow chlorine gas into the acidic, aqueous chloride solution, because of its high oxidative power, in particular viewed from reaction efficiency.

When chalcopyrite, which is leached with chlorine more slowly than chalcocite, bornite or high-quality copper matte, is the main copper sulfide to be leached out, suppressing oxidation of sulfur while securing high copper extraction is an important problem. It is preferable to adequately control oxidative power during the leaching step, in order to control sulfur oxidation. The oxidative power can be suppressed by optimizing the conditions, e.g., oxidation-reduction potential of the leaching solution,

leaching temperature, slurry concentration and chlorine concentration of the leaching solution.

Oxidation-reduction potential (sometimes referred to as ORP, based on an Ag/AgCl electrode) of the leaching solution for the chlorine-aided leaching step, although not limited, is preferably 500 to 600mV, more preferably 500 to 520mV. At below 500mV, copper extraction tends to be insufficient, because of insufficient oxidative power for the leaching step. At above 600mV, on the other hand, sulfur tends to be excessively oxidized. It should be noted that sulfur is little oxidized at an ORP of 500 to 520mV. When the raw copper material is mainly composed of chalcopyrite, the leaching is effected particularly preferably at an ORP of 500 to 520mV.

Leaching temperature, although not limited, is preferably 100 to 110°C, more preferably 105 to 110°C. At lower than 100°C, copper and iron can be leached at an insufficient rate, while sulfur is oxidized. At higher than 110°C, on the other hand, the leaching step needs a system operating at an elevated pressure.

The initial slurry concentration (concentration of the raw copper material in the slurry) for the above step, although not limited, is preferably 100 to 400g/L, more preferably 250 to 400g/L. At below 100g/L, copper and iron can be leached at an insufficient rate, while sulfur is oxidized. At above 400g/L, on the other hand, the system investment tends to be higher while the system operability tends to be lower.

The chlorine ion concentration in the leaching solution at the end of the leaching step, although not limited, is preferably 200 to 400g/L, more preferably 250 to 400g/L. At below 200g/L, copper and iron can be leached

at an insufficient rate, while sulfur is oxidized. On the other hand, the concentration has little effect for accelerating the reaction, when it is increased to above 400g/L. It is preferable to control the rate at which chlorine is blown into the acidic, aqueous chloride solution, in order to keep the chlorine ion concentration at 200 to 400g/L in the final leaching solution.

The refining process of the present invention can leach copper and iron at a rate of 95% or more and 90% or more out of a raw copper material composed mainly of chalcopyrite while keeping oxidation of sulfur in the chalcopyrite at a rate of 5% or less, when the chlorine-aided leaching step is effected under the above conditions. Therefore, it can achieve high copper extraction for chalcopyrite while suppressing oxidation of sulfur, which is one of the objects for developing hydrometallurgical copper refining processes.

The leaching product liquor containing the cupric and ferric ion, and residue containing elemental sulfur may be treated by the ordinary process for solid/liquid separation.

### 3. Copper ion reduction step

The copper ion reduction step for the refining process of the present invention treats, in the presence of a reductant, the leaching product liquor containing copper ion, iron ion and the like, discharged from the chlorine-aided leaching step to reduce these ions, the cupric ion to the cuprous ion and, at the same time, ferric ion to the ferrous ion. This allows the copper ion to be extracted selectively by an organic solvent in the subsequent solvent extraction step from the reduction product liquor in which the cuprous ion is present at a high proportion.

In the above step, the reduction product liquor is kept at an ORP (based on an Ag/AgCl electrode) at which the cupric ion present in the aqueous chloride solution containing copper and iron can be reduced into the cuprous ion. The ORP level is preferably 0 to 400mV, more preferably 0 to 380mV. At an ORP (based on an Ag/AgCl electrode) above 400mV, the copper ion partly becomes the divalent ion, which can work as an oxidant to partly oxidize the iron ion into the trivalent one, preventing formation of the reduction product liquor in which the cuprous ion is present at a high proportion. At an ORP (based on an Ag/AgCl electrode) below 0mV, on the other hand, the iron or copper ion may be reduced to the metallic state and precipitated.

Although it is difficult to accurately analyze the cuprous and cupric ion state in the leaching product liquor also containing the iron ion and the like, the relationship between the copper modality and ORP is estimated using Fig.2.

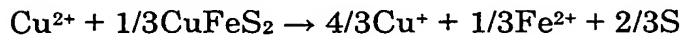
Fig.2 shows the relationship between the copper ion state (cuprous/cupric concentration ratio, Cu(1)/Cu(2)) and ORP (based on an Ag/AgCl electrode), where the chloride solution was incorporated with a varying quantity of reagent to change its ferrous ion concentration. The relationship indicates that the ORP level (based on an Ag/AgCl electrode) should be 400mV or less for the copper and iron ion to be present mostly as the cuprous and ferrous ion, respectively, and 380mV or less for these ions to be cuprous and ferrous. Therefore, in the case of a leaching product liquor which contains Cu at around 50g/L and Fe at 50 to 100g/L, the target ORP level for the reduction step is around 380 to 400mV.

The reductant for the above step, although not limited, can be at least one type selected from the group consisting of metallic copper, metals baser

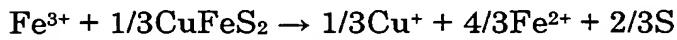
than copper, and copper sulfide and copper sulfide mineral. Of these, copper sulfide and copper sulfide mineral are particularly preferable, because they can also accelerate copper leaching. The copper and iron ion can be reduced to the monovalent and divalent state, respectively, while leaching part of the copper in a raw copper material beforehand by bringing, prior to the leaching step, the raw material containing a copper sulfide mineral into contact with the leach solution from the chlorine-aided leaching step. The resulting residue containing elemental sulfur is preferably sent to the chlorine-aided leaching step as a raw copper material to be leached therein.

When a copper sulfide mineral is chalcopyrite, the reduction reactions for converting the cupric and ferric ion into the cuprous and ferrous ion, respectively, and also for producing elemental sulfur are represented by the following chemical equations 1 and 2:

Chemical equation 1:



Chemical equation 2:



The chemical equations 1 and 2 represent the leaching reactions of chalcopyrite in the presence of the cupric and ferric ion, respectively. As shown, leaching of chalcopyrite proceeds with reduction of the cupric and ferric ion.

In the above step, the reduction condition is not limited, when a copper sulfide mineral serves as the reductant. It may be effected at the atmospheric pressure or an elevated pressure. The reduction effected at

the atmospheric pressure is more preferable, because it needs no facility to be operated at an elevated pressure. It is therefore preferable that a copper sulfide mineral is heated at the atmospheric pressure in the leaching product liquor to produce the reduced product liquor and residue containing elemental sulfur.

The reduction treatment process effected at the atmospheric pressure is not limited. For example, the reduced state in which the cuprous ion is present at a high proportion may be produced by one of the following 2 processes.

One of these processes treats a copper concentrate mainly composed of chalcopyrite as the copper sulfide mineral, prepared to have an average particle diameter (D50) of 0.5 to 60 $\mu\text{m}$  while keeping reduction temperature of the leaching product liquor at 90 to 110°C and, at the same time, at least at the level (A) given by the following formula 1:

$$\text{Formula 1: } A(\text{°C}) = 6.79 \times \ln(B) + 81.5$$

(wherein, B is an average particle diameter (D50,  $\mu\text{m}$ ), determined by the Microtrac analyzer, at a volumetric cumulative frequency of 50% of the copper concentrate). This can keep the reduction product liquor at an ORP (based on an Ag/AgCl electrode) of 400mV or less.

The other process treats a copper concentrate mainly composed of chalcopyrite as the copper sulfide mineral, prepared to have an average particle diameter (D50) of 0.5 to 60 $\mu\text{m}$  while keeping reduction temperature of the leaching product liquor at 90 to 110°C and, at the same time, at least at the level (A) given by the following formula 2:

$$\text{Formula 2: } A(\text{°C}) = 7.04 \times \ln(B) + 95.2$$

(wherein, B is an average particle diameter (D50,  $\mu\text{m}$ ), determined by the Microtrac analyzer, at a volumetric cumulative frequency of 50% of the

copper concentrate). This can keep the reduction product liquor at an ORP (based on an Ag/AgCl electrode) of 380mV or less.

Reactivity of the cupric and ferric ion in the leaching product liquor with chalcopyrite is important for decreasing oxidation-reduction potential of the reduction product liquor, and hence extent of the reduction reaction proceeding in each of the above processes. Therefore, the essential conditions for the leaching step are use of a copper concentrate mainly composed of chalcopyrite, prepared to have a specific average particle diameter (D50), and selection of an adequate reduction temperature level based on the formula 1 or 2, which is a function of D50 of the copper concentrate.

Use of a copper concentrate whose average particle size is controlled at a given level can keep the reduction product liquor at an ORP (based on an Ag/AgCl electrode) of 400mV or less, preferably 380mV or less, at which the cuprous ion prevails over the cupric ion, when the leaching product liquor is heated at a given reduction temperature level and the atmospheric pressure. This means that the cupric ion can be efficiently reduced into the cuprous ion by the treatment effected at the atmospheric pressure.

The copper concentrate for the reduction process has an average particle size (D50) of 0.5 to 60 $\mu\text{m}$ , preferably 1 to 10 $\mu\text{m}$ , more preferably 3.5 to 8.2 $\mu\text{m}$ . A concentrate having a D50 level below 0.5 $\mu\text{m}$  may cause problems, e.g., leak or deteriorated precipitation in separation of the reduction product liquor from the residue. On the other hand, a concentrate having a D50 level above 60 $\mu\text{m}$  may decrease its reactivity, needing to hold the leaching product liquor for a longer time at a higher temperature closer to its boiling point, in order to secure the target ORP

level. This should decrease productivity and energy efficiency.

The method for adjusting particle size of the copper concentrate for the reduction step is not limited. The particle size can be adjusted by various commercial crushers, e.g., agitation/crushing machine using a medium (commonly referred to as bead mill, e.g., Nano grain Mill NM-G5M supplied by Asada Iron Works or NVM-2 supplied by Aimex), and planetary ball mill (e.g., Planetary Mill SKF-04 supplied by Seishin Enterprise).

The reduction step is effected at 90 to 110°C. The leaching solution preferably contains the chloride ion at 200 to 400g/L in the chlorine-aided leaching step, which means that boiling point of the leaching product liquor increases to near 110°C. At above 110°C, the reduction step is not operable at the atmospheric pressure. At below 90°C, on the other hand, leaching efficiency is insufficient, because the reaction proceeds only slowly, even when the copper concentrate is divided finely, and the treatment needs a long time to secure the target ORP level.

The initial copper concentrate slurry concentration for the reduction step is not limited. Increasing the concentration accelerates the reduction reaction on one hand, but the optimum concentration tends to be limited by other considerations, e.g., process mass balance, and solubility of copper chloride and iron chloride. As a net, it is preferably 50 to 250g/L, at which operable limitations are minimized, more preferably around 100g/L. Practical problems are not anticipated, when the initial slurry concentration is set at around 100g/L.

In the above reduction process, the relationship between average particle size (D50) of the copper concentrate and adequate reduction

temperature is established by finding the temperature level (A) given by the following formula 1 or 2 using the (D50) level(B) of the concentrate, and setting the leaching product liquor reduction temperature at 90 to 110°C and, at the same time, at least at the temperature level (A):

$$\text{Formula 1: } A(\text{°C}) = 6.79 \times \ln(B) + 81.5$$

$$\text{Formula 2: } A(\text{°C}) = 7.04 \times \ln(B) + 95.2$$

(wherein, B is an average particle diameter (D50,  $\mu\text{m}$ ), determined by the Microtrac analyzer, at a volumetric cumulative frequency of 50% of the copper concentrate).

This can keep the reduction product liquor at the target ORP level (based on an Ag/AgCl electrode) of 400mV or less (based on the formula 1) or 380mV or less (based on the formula 2), at which the reduction product liquor containing the cuprous ion at a high proportion can be obtained.

The formula 1 or 2 represents the relationship between the D50 level of a copper concentrate and reduction temperature for securing the target ORP level (based on an Ag/AgCl electrode) of 400mV or less or 380mV or less at the initial copper concentrate slurry concentration of 100g/L. The relationship is established by the following procedure. Fig.3 shows the relationships among reduction temperature, particle size and ORP level (based on an Ag/AgCl electrode), where the reduction treatment was effected under varying reduction temperature and particle size. The approximated lines at 90, 104 and 107°C are drawn in Fig.3. The relationships among the target ORP, temperature and D50, obtained by the above procedure, are given in Table 1 and Figs. 4 and 5. The approximated lines, obtained by the regression analysis, represent the formula 1 and 2, respectively.

[Table 1]

	Target ORP (mV)							
	3 8 0				4 0 0			
D 5 0 ( $\mu$ m)	0. 5	2	3	6	4	1 2	4 5	6 0
Temperature (°C)	90	100	104	107	90	100	107	109

As discussed above, it is apparent that the reduction product liquor containing the cuprous ion at a high proportion can be produced by reducing the cupric ion to the cuprous ion by using a copper concentrate mainly composed of inexpensive chalcopyrite.

As discussed above, the copper ion reduction step for the refining process of the present invention efficiently reduces the cupric and ferric ion in an aqueous chloride solution to the cuprous and ferrous ion while suppressing oxidation of sulfur in a copper sulfide mineral, to produce the reduction product liquor containing the cuprous and ferrous ion, and residue containing elemental sulfur. Therefore, it can achieve efficient reduction of copper, which is one of the objects for developing hydrometallurgical copper refining processes.

#### 4. Solvent extraction step

The solvent extraction step for the refining process of the present invention comprises two steps; one is for contacting and mixing the reduction product liquor containing the cuprous ion, discharged from the copper ion reduction step, with the aid of an organic solvent containing an organic extractant to selectively extract the cuprous ion in the organic solvent, and the other is for contacting and mixing the organic solvent which has extracted the cuprous ion with an aqueous solution to strip the ion in the aqueous solution, to produce the aqueous solution containing the

copper ion and raffinate containing the iron ion and concomitant valuable metal ion. The reduction product liquor is kept at an ORP (based on an Ag/AgCl electrode) of 0 to 400mV.

The organic extractant for the above step is not limited, so long as it can extract the cuprous ion and thereby to separate it from iron and a concomitant valuable metal. However, a solvating extractant, e.g., tributyl phosphate, is particularly preferable. Tributyl phosphate as an extractant selectively extracts the cuprous ion in the organic solvent phase by the solvent extraction effected at an optimum oxidation-reduction potential, leaving the ferrous ion, silver ion or the like in the raffinate.

Concentration of a solvating extractant (e.g., tributyl phosphate) in the organic solvent phase, although not limited, is preferably 40 to 100% by volume, more preferably 50 to 100%. At below 40% by volume, it may not secure a copper extraction industrially expected. Tributyl phosphate is used normally after being diluted with a diluent, e.g., kerosene, to keep it fluid. However, the dilution should be avoided as far as possible to improve copper ion extraction rate, which depends on concentration of the chloride ion and that of tributyl phosphate in the reduction product liquor.

Concentration of copper in the aqueous solution for the stripping step, although not limited, is preferably 70g/L or less. Increasing the concentration beyond 70g/L may cause a phenomenon in which copper conversely moves into the organic solvent phase.

Concentration of chlorine in the aqueous solution for the stripping step, although not limited, is preferably 50 to 350g/L. At below 50g/L, the stripped cuprous ion may not be kept soluble in the solution, because of its

low solubility in water. The stripped cuprous ion is normally kept soluble in the solution by sufficiently increasing chlorine ion concentration of the solution for the stripping in consideration of concentration of the copper ion to be stripped. However, the chlorine ion concentration is limited to 350g/L, which is the practical upper limit.

Stripping temperature for the above step, although not limited, is preferably 40 to 90°C, more preferably 50 to 90°C. At below 40°C, movement of the copper ion in tributyl phosphate towards the aqueous phase may be retarded to decrease its stripping rate. At above 90°C, on the other hand, heat radiation from the solution and evaporation of the solvent tend to be excessive, making it difficult to keep system temperature at a given level, and also keep the organic solvent and aqueous phase stable.

As discussed above, the solvent extraction step for the refining process of the present invention can efficiently produce the aqueous solution containing the cuprous ion and raffinate containing the iron ion and a concomitant valuable metal from the reduction product liquor, discharged from the copper ion reduction step.

##### 5. Copper electrowinning step

The copper electrowinning step for the refining process of the present invention recovers copper by electrolyzing the stripping product liquor containing the cuprous ion, discharged from the solvent extraction step, to produce the electrolytic copper on the cathode and spent electrolyte.

The copper electrowinning method for the above step is not limited, and may be selected from the various methods which recover a metal by electrolysis from its chloride. Of these, the particularly preferable one is

diaphragm-aided electrolysis which uses an electrolysis tank composed of a cathode chamber and anode chamber separated from each other by a diaphragm, characterized in that the stripping product liquor (aqueous solution of cuprous chloride), discharged from the solvent extraction step, is supplied to the cathode chamber to electrowin copper on the cathode, the iron spent electrolyte (aqueous solution of iron chloride) composed of an aqueous iron chloride solution, discharged from the iron electrowinning step, is supplied to the anode chamber for anodic oxidation, and the solution being supplied to the anode chamber is prevented from flowing into the cathode chamber through the diaphragm. More preferably, the solution discharged from the cathode chamber is recycled back as the stripping solution to the solvent extraction step, and the solution discharged from the anode chamber is recycled back as the leachate to the chlorine-aided leaching step.

How copper is electrolyzed and recovered is described by referring to Fig.6, which illustrates one structural embodiment of the electrolysis tank for the copper electrowinning step.

The electrolysis tank shown in Fig.6 is composed of the cathode chamber 11 and anode chamber 12 separated from each other by the diaphragm 13, each chamber being equipped with the corresponding electrode. The cathode 14 is not limited, and may be of metallic copper, titanium or stainless steel. The anode 15 is also not limited, and may be of an insoluble electrode (e.g., DSE® supplied by Permelec Electrode Ltd.) which has been used for generating chlorine gas from an aqueous chloride solution in saline electrolysis or the like.

The electrolysis tank is structured in such a way to prevent the solution 19 being supplied to the anode chamber 12 from flowing into the cathode

chamber 11 through the diaphragm 13. The cathode chamber solution 20 and anode chamber solution 21 are separated from each other, but not strictly, because the diaphragm 13 should pass the ions and electricity. In other words, the structure is acceptable when it prevents free movement of the oxidized anode chamber solution 21 into the cathode chamber 11, and not necessary to completely prevent flow of the ions and water.

The diaphragm for realizing the structural feature of the electrolysis tank is not limited, and may be of filter cloth or solid electrolyte membrane. Of these, filter cloth finely woven to have a low water permeability is more preferable, because a solid electrolyte membrane is more costly and sensitive to impurities than cloth.

Water permeability of the diaphragm, although not limited, is preferably 0.04 to  $0.15\text{L}/\text{m}^2\cdot\text{s}$ . A diaphragm having a water permeability below  $0.04\text{L}/\text{m}^2\cdot\text{s}$  tends to increase tank voltage and filter cloth cost, because of limited liquid flow. A diaphragm having a permeability above  $0.15\text{ L}/\text{m}^2\cdot\text{s}$ , on the other hand, tends to decrease copper yield, because of excessive solution movement.

When contamination of the anode chamber solution 21 with a small quantity of the cathode chamber solution 20 flowing into the anode chamber 12 has little operational influence, it is preferable to keep head of the cathode chamber solution 20 higher than that of the anode chamber solution 21 to prevent flow of the anode chamber solution 21 towards the cathode chamber 11 side. More specifically, for example, the overflow level is kept slightly higher in the cathode chamber 11 than in the anode chamber 12, to prevent flow of chlorine gas and the solution containing chlorine gas in the anode chamber 12 into the cathode chamber 11 by the solution level difference.

It is necessary to equilibrate electrolysis reactions comprising reduction on the cathode and oxidation on the anode (anodic oxidation) for smoother copper electrowinning.

Therefore, the electrolysis tank is structured in such a way to send the stripping product liquor (aqueous solution of cuprous chloride), discharged from the solvent extraction step, as the cathode supply solution 18 to the cathode chamber 11 to reduce the cuprous ion on the cathode 14 and electrodeposit the metallic copper thereon, and, on completion of the reaction, to directly discharge the cathode chamber solution 20 from the cathode chamber 11 for recovery.

The electrolysis tank is also structured in such a way to send the iron spent electrolyte (aqueous solution of iron chloride) discharged from the iron electrowinning step as the anode supply solution 19 to the anode chamber 12 for anodic oxidation on the anode 15, and, on completion of the reaction, to directly discharge the anode chamber solution 21 from the anode chamber 12 for recovery. The aqueous solution of iron chloride, discharged from the iron electrowinning step, contains the ion which can be oxidized on the anode to release the electron, and hence can establish the electrolysis reaction. For example, when the reaction to oxidize ferrous chloride to ferric chloride is effected as the anodic reaction to reduce cell voltage, the solution leaving the anode in the iron electrowinning step is suitable as the anode supply solution 19 for copper electrowinning, because it is a solution of ferric chloride containing a sufficient quantity of the chlorine ion. The anodic oxidation of the aqueous solution of ferric chloride in the iron electrowinning step releases chlorine gas.

The anode chamber solution 21 is discharged after being contaminated

with part of the cathode chamber solution 20, because the solution 21 is not strictly separated from the solution 20 by the diaphragm 13. However, most of the cathode chamber solution 20 is directly discharged as the spent catholyte 22. As a result, the cuprous ion not extracted and remaining in the cathode chamber solution 20 can be recovered without being oxidized by the oxidative anode chamber solution 21. Therefore, it is suitable as the stripping solution for the solvent extraction step, because it causes no reaction-related problem.

The spent anolyte 23, which is recycled back to the chlorine-aided leaching step, causes no problem related to the liquid balance, because there is essentially no fluctuation in the solution volume in the copper electrowinning step. Moreover, ferric chloride serving as an oxidant is transformed into more oxidative chlorine gas, which is preferable for further improving efficiency of the leaching step.

The method for discharging the spent catholyte 22 or spent anolyte 23 is not limited, so long as the solution level in each chamber is kept constant. These solutions can be automatically discharged in a simple manner when the chambers are provided with an overflow port 16 and 17 matching the liquid level in each chamber.

The copper electrowinning step for the refining process of the present invention achieves high current efficiency, because of the electrowinning of the cuprous ion in the step. The cathode chamber solution produced by the step is reductive, which is a reactionally stable and suitable feature as the stripping solution for the solvent extraction step. On the other hand, the anode chamber solution is strongly oxidative, which is a suitable feature as the leaching solution for the chlorine-aided leaching step. Recycling these

solutions back to the respective step achieves the overall liquid balance for the whole process including these steps.

#### 6. Iron electrowinning step

The iron electrowinning step for the refining process of the present invention electrolyzes the raffinate discharged from the solvent extraction step and recovers iron from the residue, to produce the electrolytic iron on the cathode and anode supply solution suitable for the copper electrowinning step. The iron electrowinning step is preferable, because it provides the site for treating the residue and effective resource utilization since the electrolytic iron can be reused as pure or scrap iron.

How iron is electrolyzed and recovered in the above step is not limited. For example, it is preferable to adopt diaphragm-aided electrolysis in which the raffinate is used as the anode supply solution to produce the solution from the anode chamber. The spent anolyte is an aqueous solution of iron chloride, and can be recycled back to the chlorine-aided leaching step as the leaching solution for newly leach copper. However, it is preferably recycled back to the copper electrowinning step as the anode supply solution. In other words, it is particularly preferable, viewed from over all efficiency of the hydrometallurgical copper refining process, that the spent anolyte is supplied to the anode chamber via the copper electrowinning step and then recycled back to the chlorine-aided leaching step.

The diaphragm-aided electrolysis method is not limited. However, the one treating a specific supply solution under specific electrolysis conditions is preferable to control generation of chlorine gas and decrease cell voltage. In such a system, electrowinning of iron is controlled to an extent less than one-thirds of that for the divalent iron ion supplied to the anode chamber,

because the divalent iron is oxidized into the trivalent iron on the anode at a rate twice as high as that for the iron ion deposited on the cathode. The electrolysis sufficiently proceeds when the divalent iron is merely oxidized into the trivalent iron on the anode, and hence generation of chlorine gas is controlled. In other words, generation of chlorine gas is controlled and cell voltage is decreased in the diaphragm-aided electrolysis step by supplying the iron ion to the anode chamber at a rate at least twice as high as that for the iron deposited on the cathode.

Oxidation of the divalent iron into the trivalent one in the solvent extraction step or subsequent step, when occurs, decreases current efficiency in the iron electrowinning step to increase the power cost. Therefore, iron powder, iron plate or the like is preferably provided at the supply port for the iron electrowinning step to reduce the trivalent ion in the solution into the divalent one.

As discussed above, the diaphragm-aided electrolysis which treats a specific supply solution under specific electrolysis conditions in the iron electrowinning step forms the anode supply solution suitable for the electrolytic iron and copper electrowinning step, and, at the same time, controls generation of chlorine gas and decreases cell voltage. Therefore, it can achieve efficient recovery of iron while reducing residue wastes, which is one of the objects for developing hydrometallurgical copper refining processes.

## 7. Solution purification step

The refining process of the present invention can include, as required, the solution purification step upstream of the iron electrowinning step to treat the raffinate containing iron, discharged from the solvent extraction

step. This step is to separate the raffinate containing iron, discharged from the solvent extraction step, into the solid containing a concomitant valuable metal and purified solution containing iron by precipitating the valuable metal.

In general, iron potentially tends to form an eutectoid with another impurity in the iron electrowinning step. It is therefore necessary to remove the impurity, in order to obtain iron reusable as a resource. The solution purification step can be included to recover a concomitant valuable metal from the raffinate discharged from the solvent extraction step and obtain iron reusable as a resource.

The method for the solution purification step can be selected from known ones. Of these, at least one selected from the group consisting of sulfidation, cementation and neutralization is preferable. It can be adequately selected according to type and content of the concomitant valuable metal, which vary depending on how it is contained in the raw material and solvent extraction conditions, and cannot be specified.

The solid containing the concomitant valuable metal and purified solution containing iron, discharged from the solution purification step, are separated from each other by the ordinary solid/liquid separation method.

#### 8. Leaching residue treatment step

The refining process of the present invention may include, as required, the leaching residue treatment step, as required, to treat the residue containing elemental sulfur, discharged from the chlorine-aided leaching step. The leaching residue treatment step distills the residue containing elemental sulfur under heating in an inert atmosphere to separate the residue into the condensed sulfur and residue containing a concomitant noble metal or the like, after evaporating sulfur.

Distillation temperature, although not limited, is preferably 250 to 350°C, more preferably 330 to 350°C. At below 250°C, sulfur is evaporated insufficiently.

Sulfur condensed at the cooling section in the distillation unit in the distillation treatment may be further refined, as required, to produce a sulfur product. On the other hand, the noble metal concentrated in the residue can be recovered by a noble metal recovery system which has been adopted in the conventional refining and purification method. The residue is treated to be completely free of elemental sulfur and the noble metal contained therein can be efficiently recovered.

#### 9. Copper electrolysis/purification step

The refining process of the present invention may include, as required, the copper electrolysis/purification step which treats extracted copper produced by the copper electrowinning step, which is used as the anode to be electrolyzed and purified. This step separates the electrolytic copper into the high-purity, electrolytic copper and silver-containing slime. It is adopted, as required, when the electrolytic copper produced by the copper electrowinning step contains an impurity at a high proportion. For example, the electrolytic copper is molten and cast into the anode, which is treated by the common electrolysis/purification system to distribute the impurity and noble metal into the slime or electrolytic solution, thereby it can produce the high-purity electrolytic copper on the cathode. The electrolytic copper may be also cast into the anode by a converter or refining furnace provided in the latter stage of an existing pyrometallurgical refining process. The anode can be treated in an existing copper electrolysis/refining process.

The structure of the process scheme for the present invention, described above in detail, may be selected from the adequate ones in consideration of raw copper material composition (type and content of copper sulfide, content of iron, noble metal content and another valuable substance), quality of the recovered product, plant site, and so on. For example, when iron is present at a low content in the raw material and discharged from the system mostly in the leaching residue, in particular when the raw material is chalcocite ( $Cu_2S$ ) or high-quality copper matte, the solvent extraction, solution purification and iron recovery steps may be saved.

## EXAMPLES

The present invention is described in detail by EXAMPLES which by no means limit the present invention. The following analytical procedures and measurement procedure of average particle size (D50) were used in EXAMPLES.

- (1) Analysis of metals: ICP emission spectrometry was used, with the liquid sample analyzed directly and solid sample analyzed after it was dissolved in an acid.
- (2) Analysis of chlorine concentration: Hydrochloric acid concentration was determined by potentiometric titration with silver nitrate, and concentrations of the chlorine ion accompanying the copper, iron and sodium ions, determined by ICP emission spectrometry, were calculated, to sum up these values.
- (3) Analysis of mineral species composition and sulfur modality: These were estimated from the chemical analysis results after the mineral species was microscopically identified.
- (4) Measurement of average particle size (D50): Average particle size (D50) was determined by a Microtrac particle size distribution analyzer (Nikkiso, 9320HRA (X-100)).

(EXAMPLE 1)

(1) Chlorine-aided leaching step

A raw copper material was leached with the aid of chlorine in an acidic, aqueous solution of chloride to elute out copper in the solution to produce the leaching product liquor containing the copper ion and residue containing elemental sulfur, which were evaluated.

The chemical composition of the raw copper material is given in Table 2, and that of the copper concentrate as a mineral species composition is given in Table 3.

[Table 2]

Composition (% by weight)				Content (g/t)	
Cu	Fe	S	SiO <sub>2</sub>	Au	Ag
27.9	26.0	30.5	5.1	9	95

[Table 3]

Mineral species (% by weight)			
Chalcocite (Cu <sub>2</sub> S)	Chalcopyrite (CuFeS <sub>2</sub> )	Iron pyrite (FeS <sub>2</sub> )	Others
<0.1	85.7	4.1	10.2

A 500mL reactor of titanium was charged with a given quantity (30 to 120g) of the copper concentrate and 300mL of an acidic, aqueous solution of chloride containing copper at 60g/L and chlorine ion at 200g/L, where the slurry concentration was set at 100 to 400g/L.

The concentrate, kept at 105 to 110°C by an oil bath, was treated in the chlorine-aided leaching step with chlorine gas blown to keep the system at a constant ORP (based on an Ag/AgCl electrode) of 450 to 750mV. The

samples were collected 1, 3 and 6 hours after the treatment was started, to measure quantity of the leaching residue, and concentrations of copper ion, iron ion and sulfur in the leaching product liquor, thereby determining rates at which copper and iron were leached out of the copper concentrate and sulfur oxidation rate.

The leaching step was conducted with the initial leaching solution, prepared in such a way to have a chlorine ion concentration at 22 to 419g/L with copper chloride, iron chloride and sodium chloride, at an ORP (based on an Ag/AgCl electrode) of 520mV and 100 to 110°C.

Table 4 gives the effects of oxidation-reduction potential (ORP) on copper and iron extraction and sulfur oxidation, Fig.7 the effects of slurry concentration on copper and iron extraction, and Fig.8 the effects of the final chlorine ion concentration and copper and iron extraction and sulfur oxidation.

[Table 4]

ORP (mV)	Extraction (%)		Sulfur oxidation(%)
	Cu	Fe	
450	63.2	61.2	5.8
475	72.9	68.4	4.6
500	97.1	91.0	5.3
520	98.1	92.1	3.4
560	92.6	83.0	3.8
640	93.2	86.9	6.2
750	91.0	91.5	42

High copper and iron extraction and low sulfur oxidation can be realized by keeping the chlorine-aided leaching solution preferably at an

ORP (based on an Ag/AgCl electrode) of 500 to 600mV, more preferably 500 to 520mV (Table 4), by keeping the initial slurry concentration of the leaching solution preferably at 100 to 400g/L, more preferably 250 to 400mg/L (Fig.7), and by keeping the final chlorine ion concentration, i.e., concentration of chlorine ion in the final leaching solution, preferably at 200 to 400g/L, more preferably 250 to 400g/L (Fig.8).

## (2) Copper ion reduction step

The copper ion reduction step was carried out with Leaching Product Liquors A, B, C, D, E, F, G and H, and Copper Concentrates A, B, C, D, E and F at a given reduction temperature of 89 to 109°C following the procedure, described below, for reducing the leaching product liquor, to measure the final ORP level (based on an Ag/AgCl electrode). The results are given in Table 5. The starting ORP level (based on an Ag/AgCl electrode, 90°C) of the leaching product liquor is also given for reference.

### [Leaching product liquor]

- (1) Composition: Each of Leaching Product Liquors contained copper, iron and chloride ion at 30, 100 and 220g/L, respectively.
- (2) Initial ORP (based on an Ag/AgCl electrode, 90°C)  
A: 508mV, B: 490mV, C: 481mV, D: 482mV, E: 490mV, F: 491mV, G: 495mV and H: 498mV

### [Copper concentrate]

- A: Copper Concentrate A (D50: 60 $\mu$ m, Chemical composition: 26% of copper, 29% of iron, 28% of sulfur and 17% of others, all percentages being by weight)
- B: Copper Concentrate A dry-crushed by a planetary ball mill (Planetary Mill SKF-04 supplied by Seishin Enterprise) to have a D50 value of 3.77 $\mu$ m,

where Copper Concentrate A was ball-milled in a vessel filled with 8mm-diameter steel balls to 50% of the volume at 150rpm for 1 hour.

C: Copper Concentrate A wet-crushed by a beads mill (Nano mill NM-G5M supplied by Asada Iron Works) to have a D<sub>50</sub> value of 1.08 $\mu$ m, where Copper Concentrate A was slurried with water to have a concentration of 100g/L and passed 3 times through the crushing chamber of the beads mill.

D: Copper Concentrate A wet-crushed by a beads mill (Nano mill NM-G5M supplied by Asada Iron Works) to have a D<sub>50</sub> value of 1.33 $\mu$ m, where Copper Concentrate A was slurried with water to have a concentration of 100g/L and passed 2 times through the crushing chamber of the beads mill.

E: Copper Concentrate A wet-crushed by a beads mill (Nano mill NM-G5M supplied by Asada Iron Works) to have a D<sub>50</sub> value of 2.21 $\mu$ m, where Copper Concentrate A was slurried with water to have a concentration of 100g/L and passed once through the crushing chamber of the beads mill.

F: Copper Concentrate A wet-crushed by a beads mill (Nano mill NM-G5M supplied by Asada Iron Works) to have a D<sub>50</sub> value of 0.76 $\mu$ m, where Copper Concentrate A was slurried with water to have a concentration of 100g/L and circulated in the crushing chamber of the beads mill for 1 hour.

#### [Procedure for reducing the leaching product liquor]

The leaching product liquor of given composition was mixed with 50g of the copper concentrate prepared to have a given average particle size (D<sub>50</sub>) in a 500mL glass beaker in such a way to have an initial slurry concentration of 100g/L, and heated with stirring to a given reduction temperature, at which the mixture was held for 3 hours.

[Table 5]

No.	Leaching product liquor case	Copper concentrate		Reduction temperature (°C)	ORP (mV)	
		case	D 5 0 ( $\mu$ m)		Initial solution	Final solution
1	A	B	3. 7 7	1 0 7	5 0 8	3 7 5
2	B	B	3. 7 7	1 0 4	4 9 0	3 8 2
3	C	A	6 0	1 0 9	4 8 1	3 9 5
4	C	C	1. 0 8	9 2	4 8 1	3 8 8
5	C	D	1. 3 3	9 1	4 8 1	3 9 2
6	C	E	2. 2 1	9 0	4 8 1	4 0 0
7	C	F	0. 7 6	9 2	4 8 1	3 8 3
8	D	A	6 0	8 9	4 8 2	4 3 0
9	E	A	6 0	9 8	4 9 0	4 1 3
10	F	A	6 0	1 0 1	4 9 1	4 1 3
11	G	A	6 0	1 0 4	4 9 5	4 0 9
12	H	A	6 0	1 0 6. 5	4 9 8	4 0 4

As shown in Table 5, an ORP level (based on an Ag/AgCl electrode) of 400mV or less can be attained, when reduction temperature is controlled for the leaching product liquor at 90 to 110°C and at least (A) which satisfies the formula 1 as a function of D50 of the copper concentrate used, as shown in Table 5 (Run No.1 to 7). Particularly noted is that the level of 380mV or less can be attained, when the temperature is controlled at least at (A) which satisfies the formula 2 (run No.1). By contrast, it is noted that an ORP level (based on an Ag/AgCl electrode) of 400mV or less cannot be attained, when the reduction temperature fails to satisfy the formula 1 or 2, which represents the relationship between D50 of the copper concentrate and reduction temperature (Run No.8 to 12). It is therefore preferable to control reduction temperature at least at the level (A) given by the formula

1 or 2.

(3) Solvent extraction step

Leaching Product Liquors A, B, C and D were treated by the solvent extraction step to extract copper, which was then treated by the stripping step to produce the stripping product liquor containing the cuprous ion and raffinate containing the ferrous ion. These stripping product streams were evaluated.

The reduction product liquor containing Cu and Fe at 75 and 51g/L, prepared in the above step was used as Reduction Product Liquor A, where 500mL of the solution was incorporated with powdered copper to have an ORP (based on an Ag/AgCl electrode) of 300mV, to completely reduce the copper ion in the solution into the monovalent state. The resulting solution was used as the initial solution for the solvent extraction step, where the solution was incorporated with 500mL of tributyl phosphate (Daihachi Chemical Industry, TBP®) diluted with an diluent (Showa-Shell, SHELLSOL A) to have a concentration of 40% by volume, and the mixture was shaked at 50°C for 10 minutes for the solvent extraction to produce the organic solvent phase and aqueous phase. Then, the organic phase was stripped with 250mL of water, controlled at pH 1 with hydrochloric acid, with shaking for 10 minutes.

Table 6 gives the compositions of the stripping product liquor, initial solution for the solvent extraction step and raffinate.

[Table 6]

Solvent extraction	Cu and Fe concentrations (g/L)	
	C u	F e
Initial solution	75	51
Raffinate	13	48
Stripping product liquor	31	4

Use of tributyl phosphate as the extractant efficiently separates copper selectively over iron, as shown in Table 6.

The solvent extraction step was carried out for the synthetic aqueous solution containing cupric chloride and ferric chloride at 80 and 50g/L as Cu and Fe (Reduction Product Liquor B), where the solution was incorporated with sodium chloride to have a chlorine ion concentration of 200g/L, and further incorporated with powdered iron at 60°C to have an ORP (based on an Ag/AgCl electrode) of 300mV. The resulting solution was brought into contact at room temperature with an organic solvent diluted with kerosene to have a given tributyl phosphate concentration of 40 to 100% by volume, to extract the metallic ions into the tributyl phosphate, in an inert atmosphere of nitrogen to prevent oxidation at the gas/liquid interface. The copper and iron extraction were determined. The results are given in Figs.9 and 10.

Increasing tributyl phosphate concentration increases copper extraction, but changes iron extraction to only a limited extent, as shown in Fig.9. Increasing tributyl phosphate concentration also improves copper/iron separation coefficient, as shown in Fig.10.

The solvent extraction step was carried out for the solution containing cupric chloride, ferric chloride and silver chloride at 118g/L, 90g/L and 9mg/L as Cu, Fe and Ag (Reduction Product Liquor C), where the solution was incorporated with powdered iron at 60°C to have an ORP (based on an Ag/AgCl electrode) of 300mV. The resulting solution was brought into contact at room temperature with tributyl phosphate to extract the metallic ions thereinto, in an inert atmosphere of nitrogen to prevent oxidation at the gas/liquid interface. Then, the resulting solution was stripped with a stripping solution controlled at pH 1.0 with hydrochloric acid and a chlorine ion concentration at 50g/L with sodium chloride, to strip the copper ion in the tributyl phosphate at 50°C. The raffinate and stripping product liquor were analyzed for their Cu, Fe and Ag concentrations.

The raffinate contained Cu, Fe and Ag at 60g/L, 90g/L and 8mg/L, and the stripping product liquor contained Cu, Fe and Ag at 28g/L, 5g/L and 1mg/L or less, by which was meant that silver was not extracted into tributyl phosphate but left in the raffinate, and copper and silver were separated almost completely.

The solvent extraction step was carried out for the synthetic aqueous solution containing cupric chloride and ferric chloride at 50 and 70g/L as Cu and Fe (Reduction Product Liquor D), where the solution was incorporated with sodium chloride to have a chlorine ion concentration of 200g/L, and further incorporated with powdered iron at 60°C to have an ORP (based on an Ag/AgCl electrode) of 275mV. The resulting solution was brought into contact at room temperature with tributyl phosphate, to extract the metallic ions into the tributyl phosphate, in an inert atmosphere of nitrogen to prevent oxidation at the gas/liquid interface. Then, the resulting solution was stripped with a stripping solution controlled at pH 0.5 with

hydrochloric acid and a chlorine ion concentration at 100g/L with sodium chloride, to strip the copper ion in the tributyl phosphate at 30, 40, 60 and 75°C. The Cu was analyzed to find stripping rate for each run. The results are given in Fig.11.

Increasing stripping temperature increases stripping rate, preferably to 50°C or higher to strip copper present in tributyl phosphate at 50% or more.

#### (4) Copper electrowinning step

The copper electrowinning step was carried out for the stripping product liquor by the following diaphragm-aided electrolysis tank to produce the electrolytic copper and spent electrolyte, which were evaluated.

Fig.6 illustrates the diaphragm-aided electrolysis tank structure, where the anode was a 70 by 70mm insoluble electrode (DSE® supplied by Permelec Electrode) and cathode was a 60 by 65mm pure copper plate. The cathode and anode chambers were separated by a filter cloth of TETRON® with fine texture and low water permeability (water permeability: 0.06L/m<sup>2</sup>·s) as the diaphragm. Each of these chambers was provided with an overflow type discharge port to independently discharge the solution, where the overflow level was kept slightly higher in the cathode chamber than in the anode chamber, to prevent flow of chlorine gas and the solution containing chlorine gas in the anode chamber into the cathode chamber by the solution level difference.

The cathode chamber in the electrolysis tank was supplied with an aqueous solution of cuprous chloride containing copper at 80g/L at a rate of 2.5mL/minute, while the anode chamber with an aqueous solution of ferric chloride containing iron at 80g/L, where the aqueous solution of cuprous chloride was kept at an ORP (based on an Ag/AgCl electrode) of 309mV.

The copper electrowinning step was carried out at a current density of 308A/m<sup>2</sup> by passing current of around 1.2A. A current efficiency from the electrolytic copper was 93%, which is equivalent to that associated with the common electrolysis of cuprous chloride (85 to 95%). A total of 25.5mL of the solution was supplied to the cathode chamber for 10 minutes, and 25.2mL of the solution was discharged from the chamber, a cathode chamber solution recovery rate of 99%. In other words, only a small quantity of the solution flowed from the cathode chamber into the anode chamber, whereas it is judged that no flow occurred in the opposite direction. The solution discharged from the cathode chamber was at an ORP (based on an Ag/AgCl electrode) of 307mV, and the cathode chamber solution had essentially unchanged properties, except for consumption of the copper ion. This means that the solution supplied to the cathode chamber can be recovered essentially totally except for decreased copper ion content, and that the solution discharged from the chamber is suitable as the stripping solution for the solvent extraction step.

The aqueous solution of ferric chloride having an ORP (based on an Ag/AgCl electrode) of 600mV was supplied to the anode chamber, where it was strongly oxidized on the anode to produce chlorine gas and, at the same time, increase ORP (based on an Ag/AgCl electrode) of the discharged solution to 900mV or more. Therefore, recycling the solution discharged from the anode chamber and chlorine gas back to the chlorine-aided leaching step produces a high oxidation power.

The analysis results of the electrolytic copper produced by the copper electrowinning step are given in Table 7. As shown, the step produced 99.99% pure (by weight) electrolytic copper containing trace quantities of

impurities.

[Table 7]

Cu purity (% by weight)	Impurity contents (ppm)						
	Fe	Ag	As	Sb	Pb	Zn	Ni
99.99	<10	<10	10	<10	<10	<50	<50

### (5) Solution purification step

The raffinate discharged from the solvent extraction step contains copper at 2 to 5g/L, and a number of concomitant valuable metals, e.g., arsenic, antimony, nickel, zinc, lead and cadmium at around 0.5g/L, and silver at around 0.1g/L, in addition to iron. These concomitant metals are impurities for the recovery of iron.

The raffinate was cleaned by sulfidation, cementation and neutralization at 50°C for 1 hour for each method. It was neutralized with slaked lime to have a pH level of 3 for the neutralization; incorporated with an aqueous solution of sodium hydrosulfide in a quantity 2 to 5 times of the equivalent needed for sulfidation of the impurities at pH 0.5 for the sulfidation; and incorporated with powdered iron to control its ORP level (based on an Ag/AgCl electrode), and treated at pH 1.4 and ORP of -71mV or pH 1.1 and ORP of -250mV for the cementation. The element removal rates by the purification step are given in Table 8.

[Table 8]

Treatment method	Conditions	Removal rates (%)						
		Cu	Fe	As	Sb	Ni	Ag	Zn
Neutralization	pH3	0	6	100	100	1	24	0
Cementation	pH1.4	45	0	13	82	2	100	0
	ORP-71mV	92	0	61	100	2	100	0
Sulfidation	ORP-250mV	pH0.5	100	1	—	100	64	100
	pH0.5	Twice the equivalent	—	—	—	—	21	97
	5 times of the equivalent	100	4	—	100	94	100	42
							100	100

(-: Not analyzed)

These impurities can be efficiently removed by each solution purification method, as shown in Table 8. For example, the neutralization can remove arsenic or antimony, sulfidation is suitable for removal of lead or nickel, and cementation or sulfidation is effective for recovering silver. The solution purification step may use a method adequately selected depending on impurities present in the copper concentrate, and does not always need all of these methods.

The impurity can be selectively separated and recovered in compound suitable for effective utilization or treatment by adequately selecting one or more of these methods.

#### (6) Iron electrowinning step

The iron electrowinning step was carried out for the iron-containing purified solution treated by the solution purification step, to evaluate the solution.

The electrolysis tank, 500mL in inner volume, was provided with an insoluble anode electrode (e.g., DSE® supplied by Permelec Electrode) having an electrode area of 60 by 60mm and cathode (titanium plate) masked to have the same electrode area, 60mm apart from each other.

The electrowinning step was carried out by passing current through the supply solution, pumped to the cathode partitioned by a filter cloth at 1 or 5mL/minute, to have a current density of 200A/m<sup>2</sup>. The discharged electrolytic solution was not reused but directly stored in a spare tank. Iron was theoretically extracted at 1.5g/hour. The iron ion was carried by the solution at 1.5g/hour when the solution was supplied at 1mL/minute, and at 7.5g/hour when the solution was supplied at 5mL/minute. These rates corresponded to the same as, and 5 times higher than, the rate at which copper is theoretically extracted.

The deposited cathode was cleaned after electrowinning for 5 hours, to determine deposited amount and current efficiency. The treatment was found to be carried out at a current density of 97%.

Cell voltage was 2.9V when the solution was supplied at 1mL/minute, and generation of chlorine gas from the anode was visually observed. When it was supplied at 5mL/minute, on the other hand, no chlorine gas generation from the anode was observed, while cell voltage was decreased to 2.3V. As discussed above, it is demonstrated that the electrolysis step of the present invention can decrease power cost.

#### (7) Leaching residue treatment step

The leaching residue treatment step was carried out by distilling the residue from the chlorine-aided leaching step to separate elemental sulfur and recover the residue containing a noble metal, where 150g of the residue put in a quartz boat was heated in a tubular furnace at 320°C in a flow of nitrogen. The gaseous stream was air-cooled by a cooling tube provided at the gas discharge port. The heating was continued for 4 hours, and the system was allowed to cool in a flow of nitrogen. Then, the residue and sulfur were withdrawn when furnace inside temperature was decreased to 70°C or lower. Table 9 gives chemical analysis results of the leaching residue before and after the sulfur removal treatment, and sulfur modality analysis results.

[Table 9]

Leaching residue	Chemical composition						Sulfur modality (% by weight)		
	(% by weight)				(g/t)		CuFeS <sub>2</sub>	FeS <sub>2</sub>	S <sup>0</sup>
	Cu	Fe	S	SiO <sub>2</sub>	Au	Ag			
Before sulfur removal treatment	4.2	13.5	54.9	—	47	—	12.8	20.4	47.4
After sulfur removal treatment	6.3	19.2	30.2	27.8	63	34	18.3	28.8	8.3

(—: Not analyzed)

The leaching residue treatment step removed sulfur from the feed stream, to concentrate the gold present in the residue by that extent, as shown in Table 9.

#### Advantage of the Invention

As discussed above, the process of the present invention for refining a raw copper material containing a copper sulfide mineral can be used as a hydrometallurgical refining process for a raw copper material containing a copper sulfide mineral, is useful as a process for leaching copper to recover it by the monovalent copper electrolysis while suppressing oxidation of sulfur in the raw material, as a process for recovering and effectively utilizing a concomitant valuable metal and as a process for minimizing production of wastes, e.g., leaching residue, as far as possible, and particularly suitable for refining chalcopyrite, which is known as a compound difficult to leach.